

NON-FOIL BARRIER LAMINATES

Related Applications

This application relates to Serial No. 10/288,841 which is a continuation-in-part of application Serial No. 10/105,713 filed March 25, 2002.

Field of the Invention

The present invention relates to paperboard laminates and more particularly to non-foil paperboard laminates useful for making containers for products such as fruit and citrus juices and other beverages, as well as non-liquid dry products, wherein the laminate has good barrier characteristics including the ability to prevent the transmission of oxygen which leads to the loss of Vitamin C, aroma/flavor components and other ingredients of fruit and citrus juices and other beverages packaged therein. The laminates also are effective in minimizing microbial growth by virtue of their reduced permeability to oxygen. More particularly, this invention relates to such non-foil barrier laminates intended for making containers known in the trade as "gable top" containers or other cartons to be used for products that are conventionally hot filled such as fruit juices or punches. Such filled cartons are stored at ambient conditions for a shelf life of 3-6 months before product quality is compromised.

Background of the Invention

Paperboard coated with low-density polyethylene (LDPE) has been used to make beverage containers, but falls short in providing an acceptable container for some products such as fruit juices. In particular, paperboard coated with LDPE has a relatively high permeability to oxygen which may lead to loss of flavor components and vitamins through oxidation during storage. Flavor loss can also occur as a result of migration or uptake of flavor components into the LDPE layer, a process referred to as "scalping."

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The oxidative loss of vitamins and in particular Vitamin C can be substantially reduced by the use of a laminate containing a metal foil as an oxygen barrier liner along the interior of the container. However, the economics involved in using a metal foil often require a price premium that limits profitability. Further, metal foil laminates are prone to develop pin holes, seriously affecting their ability to contain liquids. A search for economical alternatives to foil has resulted in the development of laminate structures utilizing coextruded polymer materials such as polyethylene terephthalate (PET), polyvinyl chlorides, polyvinylidene chloride (PVdC) and ethylene vinyl alcohol copolymer (EVOH) as the barrier material and in particular EVOH (to provide protection against the transfer of oxygen and aid in retention of ascorbic acid and d-limonene in citrus juice).

In addition to being less expensive than foil-containing structures, paperboard laminates containing such barrier materials may exhibit superior flavor retention properties due to the use of lower levels of LDPE as the product contact layer. Many conventional commercial structures for a paperboard carton for juice, punch and similar products now utilize a laminate containing ethylene vinyl alcohol copolymer as a barrier to oxygen and to prevent flavor and vitamin loss.

Nylon has also been proposed and used commercially as a barrier polymer in a paperboard container. It has been found not only to provide an effective barrier to oxygen but also to provide thermal resistance, mechanical strength and durability. As such, it serves as an abuse-resistant layer in the construction of laminates.

In order to ensure adequate or extended shelf life during storage, distribution and retail display under high as well as low humidity conditions, i.e., to provide a laminate with good oxygen barrier properties at relatively high humidity where EVOH is especially susceptible to degradation in barrier properties as a result of the presence of moisture, the combination of nylon and EVOH has been proposed as nylon has good barrier properties even at higher humidity conditions. Whereas nylon alone offers unacceptable barrier properties, the combination with EVOH achieves improved barrier properties of the laminates.

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As can be appreciated, considerable effort has been devoted to finding the best layer structure in a barrier laminate for a juice, punch or other beverage carton. Thus other laminate structures utilizing coextruded polymer material such as polypropylene, polyethylene terephthalates, polyvinyl chlorides, polyvinylidene chloride, ethylene vinyl alcohol, and other polymeric materials as the barrier material to provide protection against the transfer of oxygen have also been proposed.

It is an object of the present invention to provide an improved, heat-sealable laminate material for a beverage carton which does not transmit flavor/odor ingredients of citrus and other juices and punches, exhibits a substantial oxygen barrier, decreases substantially the loss of Vitamin C, flavor, and aroma, minimizes microbial growth, has performance equal to or better than that of conventionally-used polymer barrier laminates, and reduces or eliminates manufacturing difficulties without detrimental economics.

It is a further object of the present invention to provide a beverage carton constructed of a laminate effective to prevent the intrusion of oxygen into the carton and therewith the oxygen degradation of flavor and vitamin components, particularly Vitamin C, and the migration, i.e., scalping, of flavor and aroma ingredients of the beverage.

Another object of the invention is to provide a heat-sealable laminate having a low oxygen permeability during filling over a range of temperatures (cold fill to hot fill), at both room temperature and refrigerated storage conditions and under both low and high humidity conditions.

Summary of the Invention

In accordance with one embodiment of the present invention, improved heat-sealable non-foil laminates for fruit or citrus juices, punches, other beverages and the like providing an effective barrier to the intrusion of oxygen and migration of flavors and for retention of Vitamin C, flavors and aromas are provided which comprise from the paperboard surface to the inner surface which contacts the contents of the carton fabricated from the laminate, a paperboard substrate having an interior and exterior surface, a first

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layer of polyolefin coated on the exterior surface of the substrate, a first polyamide layer applied onto the interior surface of the substrate, a first oxygen barrier layer of EVOH applied directly onto the first polyamide layer, a second polyamide layer applied directly onto said first EVOH layer, a first tie layer applied directly onto the polyamide layer, a second oxygen barrier layer of EVOH applied directly onto the first tie layer, a second tie layer applied directly onto the second EVOH layer, and an innermost layer of polyolefin that will contact the contents of the container.

In another embodiment of the invention, a laminate structure for paperboard cartons or containers having the properties just described comprises paperboard which is coated with an outer layer of polyolefin, a first polyamide layer provided onto the inner surface of the paperboard, a first layer of EVOH applied directly onto the first polyamide layer, a second polyamide layer applied directly onto the first EVOH layer, a first tie layer applied directly onto the second polyamide layer, a layer of polyolefin coated onto the first tie layer, a second tie layer applied onto the polyolefin layer, a second EVOH layer coated onto the second tie layer, a third tie layer applied directly onto the second EVOH layer and an innermost layer of polyolefin applied directly onto the third tie layer, the innermost layer of polyolefin serving as the contact layer with the contents of the carton. The ultimate structure of this embodiment is essentially the same as that of the embodiment described above, but an extra tie and olefin layer are included between the second polyamide and second EVOH layer.

The polyamide layers provide strength, heat resistance and mechanical toughness around the first EVOH oxygen barrier layer during conversion of the laminate into the carton and during use. The second EVOH layer which is incorporated into the laminate closer to the juice, punch or other beverage product contact surface, enhances the overall oxygen barrier properties while limiting flavor and aroma migration or scalping.

Cartons can be constructed easily from the laminates of the present invention and provide excellent gas-barrier protection for liquid and dry products and significant flavor retention and prevention of loss of Vitamin C from the juices and

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punches contained therein, resulting in extended shelf life for such products. Moreover, carton blanks prepared from laminates of the present invention exhibit better runnability on equipment used for folding carton blanks compared to carton blanks comprising laminates having a foil barrier layer, thereby further facilitating the manufacturing process.

Brief Description of the Drawings

Fig. 1 is a schematic cross-sectional illustration showing a barrier-board laminate according to the invention.

Fig. 2 is a schematic cross-sectional illustration showing another form of barrier-board laminate according to the invention.

Fig. 3 is a graphic representation of % vitamin C retained vs. days after filling for cartons that were cold filled with orange juice and stored at 38°F for 64 days.

Fig. 4 is a graphic representation of % vitamin C retained vs. days after filling for cartons that were cold filled with orange juice and stored at 73°F for 64 days.

Detailed Description

The laminate in **Fig. 1** comprises a carrier layer or substrate **12** of paperboard (100-300 lbs.*) onto which there is applied on one side an extrusion coating of polyolefin polymer layer **11** such as LDPE, HDPE, LLDPE, metallocene or the like, preferably LDPE, at a coating weight of 9-20 lbs. and preferably about 12-15 lbs. to provide the outer surface of the laminate. Layer **11** is the outer "gloss" layer.

On the interior side of the substrate **12**, there is applied a first polyamide layer **13** at a coating weight of 1-15 lbs. and preferably about 5-10 lbs. The polyamide layer can be but is not limited to nylon 6, nylon 66, nylon 10, nylon 6-10, nylon 12, amorphous nylons, MXD-6, nylon nanocomposites and other suitable polyamides. Onto the interior surface of the polyamide layer **13**, there is applied a first oxygen barrier layer

* lbs./ream (Ream size = 3,000 sq. feet)

of EVOH copolymer **14** having a coating weight of 1-10 lbs. and preferably 3-6 lbs. The EVOH copolymer may contain 26-44 mole % ethylene. Layer 14 can also be, but is not limited to, oxygen scavenging EVOH materials, EVOH nanocomposites, or blends of EVOH with polyolefins such as low density polyethylene. Layer **15** is a second layer of polyamide and is applied in an amount of 1-15 lbs. preferably about 5-10 lbs. to the underside of the first EVOH layer. All of the materials listed for layer **13** may also be used in layer **15**.

A tie layer **16** is applied onto the inner side of the second polyamide layer **15** in an amount of 1-15 lbs. preferably 5-10 lbs. The tie layer is preferably based on, but is not limited to, ethylene based copolymers modified with maleic anhydride functional groups such as Plexar and Bynel, but can also include other common tie resins such as Nucrel, Primacor and Surllyn. Plexar 5125 is a preferred tie material. There is thereafter applied to the underside of the tie layer **16**, a layer of polyolefin **17**. The polyolefin **17** is applied in an amount of 1- 20 lbs., preferably about 4-10 lbs. The polyolefin is preferably polyethylene and most preferably a low density polyethylene. A second tie layer **18** is applied in an amount of 1-15 lbs. onto the underside of the polyolefin layer **17**. A second oxygen barrier layer of EVOH **19** in an amount of 1-10 lbs. and preferably about 3-6 lbs. is applied onto the second tie layer **18**. Layer **19** can be, but is not limited to, ethylene vinyl alcohol copolymers (containing 26-44 mole % ethylene), oxygen scavenging EVOH materials, EVOH nanocomposites, EVOH combined with inorganic fillers (such as talc or kaolin), or blends of EVOH with other polymers (such that EVOH remains the continuous phase); polyvinyl alcohols (PVOH); polyamides such as, but not limited to, nylon 6, nylon 66, nylon 6/9, nylon 10, nylon 6-10, nylon 11, nylon 12, amorphous nylons, MXD-6, nylon nanocomposites, nylon combined with inorganic fillers (such as talc or kaolin), and blends of nylon with other polymers (such that the nylon remains the continuous phase); polyethylene terephthalates including glycol-modified polyethylene terephthalates, acid-modified polyethylene terephthalates, PET nanocomposites, PET combined with other inorganic fillers (such as talc or kaolin), and blends of PET with other polymers (such that the PET remains the continuous phase); PEN; vinylidene chloride copolymer; polyvinyl

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chloride polymers; polyolefins including, but not limited to, low density polyethylene, high density polyethylene, linear low density polyethylene, polypropylene, cyclic olefin copolymers, and blends thereof; polycarbonates; and liquid crystal polymers. In addition, desiccants, molecular sieves, and the like may be added to layer **19** to improve water vapor barrier characteristics of the layer; and molecular sieves, cyclodextrins, and the like may be added to same layer for improved flavor/aroma barrier. A third tie layer **20** in an amount of 1-5 lbs. is included between the second EVOH layer **19** and the innermost layer of polyolefin **21** which is applied in an amount of 1- 20 lbs. and preferably about 4-10 lbs. The polyolefin layers **17** and **21** can be, but are not limited to, low density polyethylene, linear low density polyethylene, high density polyethylene, polypropylene, cyclic olefin copolymers, and blends thereof.

Looking at **Fig. 2**, another embodiment of the invention, the structure has a paperboard substrate **32** (100-300 lbs.) onto one side of which a coating of polyolefin **31** such as LDPE, HDPE, LLDPE, metallocene, or a blend thereof is applied in an amount of 9-20 lbs. and preferably about 12 lbs. Layer **31** is the "gloss" layer which contacts the atmosphere. A layer **33** of polyamide in a coating weight of between 1-15 lbs. and preferably about 5-10 lbs. is applied onto the underside or interior portion of the substrate **32**. The polyamide layer can be but is not limited to nylon 6, nylon 66, nylon 10, nylon 6-10, nylon 12, amorphous nylons, MXD-6, nylon nanocomposites and other suitable polyamides. The underside or the interior of the polyamide layer **33** has an EVOH layer **34** coated thereon of thickness 1-10 lbs. and preferably about 3-6 lbs. The EVOH layer can be but is not limited to EVOH containing 26-44 mole % ethylene, EVOH nanocomposites, oxygen scavenging EVOH, or blends of EVOH with polyolefins such as low density polyethylene. The EVOH layer **34** has another or second polyamide layer **35** on its underside or interior, which has a coating weight of between 1-15 lbs. and preferably about 5-10 lbs. All of the materials listed for layer **33** may also be used in layer **35**. A first tie layer **36** having a coating weight of 1-10 lbs., preferably about 4-7 lbs., is disposed on the underside of the polyamide layer **35**. A second EVOH layer **37** is applied onto the underside of the first tie layer **36** and has a coating weight of between 1-10 lbs., preferably

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3-6 lbs. The second EVOH layer can be, but is not limited to, ethylene vinyl alcohol copolymers (containing 26-44 mole % ethylene), oxygen scavenging EVOH materials, EVOH nanocomposites, EVOH combined with inorganic fillers (such as talc or kaolin), or blends of EVOH with other polymers (such that EVOH remains the continuous phase); or blends of polyvinyl alcohols (PVOH); polyamides such as, but not limited to, nylon 6, nylon 66, nylon 6/9, nylon 10, nylon 6-10, nylon 11, nylon 12, amorphous nylons, MXD-6, nylon nanocomposites, nylon combined with inorganic fillers (such as talc or kaolin), and blends of nylon with other polymers (such that the nylon remains the continuous phase); polyethylene terephthalates including glycol-modified polyethylene terephthalates, acid-modified polyethylene terephthalates, PET nanocomposites, PET combined with other inorganic fillers (such as talc or kaolin), and blends of PET with other polymers (such that the PET remains the continuous phase); polyethylene naphthalate PEN; vinylidene chloride copolymer; polyvinyl chloride polymers; polyolefins including, but not limited to, low density polyethylene, high density polyethylene, linear low density polyethylene, polypropylene, cyclic olefin copolymers, and blends thereof; polycarbonates; and liquid crystal polymers. In addition, desiccants, molecular sieves, and the like may be added to layer 37 to improve water vapor barrier characteristics of the layer; and molecular sieves, cyclodextrins, and the like may be added to same layer for improved flavor/aroma barrier. The second EVOH layer 37 has another or second tie layer 38 on its underside or interior, which has a coating weight of between 1-10 lbs. and is preferably about 4-7 lbs. Finally, a layer of polyolefin polymer 39 such as low density polyethylene, linear low density polyethylene, high density polyethylene, polypropylene, cyclic olefin copolymers, or a blend thereof, is disposed on the product side on the underside of the second tie layer 38. The product side polyolefin layer 39 has a coating weight of between 1-40 lbs. and preferably 8-22 lbs.

The embodiment of **Fig. 1** can be prepared as follows. First a layer of polyolefin 11 is extrusion coated on the outer surface of the substrate 12. There is then coextruded onto the inner surface of the substrate a four-layer sandwich of polyamide

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13/EVOH 14/polyamide 15/tie 16. A five-layer sandwich of polyolefin 17/tie 18/EVOH 19/ tie 20/polyolefin 21 is coextruded onto the inner surface of the four-layer sandwich.

In the second embodiment of the invention shown in **Fig. 2**, a layer of polyolefin **31** is extrusion coated onto the paperboard substrate **32** to provide the outer surface of the laminate. A three-layer sandwich of polyamide **33**/EVOH **34**/polyamide **35** is coextruded directly onto the inner surface of the paperboard substrate **32**. A three-layer sandwich of EVOH **37** surrounded by two tie layers **36** and **38** is coextruded onto the polyamide layer **35** of the polyamide/EVOH/polyamide coextrusion. Finally, a product contact layer **39** of polyolefin is extruded onto the inner surface of tie layer **38** of that coextrusion.

Olefin polymers suitable for use in the present invention are heat-sealable and include polypropylene, high density polyethylene, medium density polyethylene, low density polyethylene, and linear low density polyethylene and combinations thereof. Most preferred is low density polyethylene. Any commercial extrusion coating grade polyolefin is suitable for use herein. The olefin polymers may include additives to provide desired flow, adhesion or heat-sealing characteristics.

Paperboard for use in the present invention includes suitably high grade paperboard stock, for example, milk carton stock. The board may have a basis weight of about 100 to 300 lbs./ream, preferably 150 to about 200lbs./ream. Either or both paperboard surfaces can be flame or corona treated and/or primed to facilitate adhesion of subsequent polymer layers. Primers which may be used include polyethylene imine (PEI) or ethylene vinyl acetate.

The nylon used in the present invention should be suitable for coextrusion coating onto the paperboard substrate. Examples of nylons for use herein include polyamides or copolyamides such as nylon 6, nylon 6,12 (the polycondensation product of hexamethylene diamine and a 12-carbon dibasic acid); nylon 12 (the polymerization product of lauric lactam or cyclododecalactam, with 11 methylene units between the

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linking —NH—CO— groups in the polymer chain); nylon 11 (the polycondensation product of the monomer 11-aminoundecanoic acid);; nylon 6,10 (polyhexamethylene sebacamide) and amorphous nylons.

Tie layer resins suitable for coextruding with the nylon in accordance with the invention include resins which have good adhesion to both nylons and polyolefins. Preferred tie layer resins having suitable adhesion properties include anhydride-modified copolymers, especially anhydride modified ethylene copolymers. Most preferred are anhydride modified linear low/low density ethylene copolymers. An anhydride modified linear low/low density ethylene copolymer particularly suitable for use as the tie layer material in the present invention is Bynel E388 available from the duPont Corporation of America. Another duPont product, an anhydride modified ethylene acetate copolymer (Bynel E369) may also be used as the tie layer material. Other suitable tie layer materials are those described in U.S. Pat. Nos. 4,087,587 and 4,087,588, both of which are incorporated herein by reference. Materials of the type described therein are sold under the trade name Plexar.

The laminate of the invention produces an extended long life, low oxygen permeable, leak free container laminate structure such as a paperboard based package or carton that prevents the transmission of gases, in particular oxygen, therethrough, and in addition, prevents the escape of flavor components, or the ingress of microbiological contaminants and further produces such a package that is economical on a per-package cost basis, is fundamentally compatible with existing converting machinery, and can be formed, cold or hot filled, and sealed at economically high speeds using conventional packaging machine temperatures, pressures and dwell times.

The following example is provided for further illustration of the invention.

Example 1:

A non-foil barrier laminate consistent with the structure shown in **Fig. 1** was produced using 5 lbs/ream nylon 6 in layer **13**, 6 lbs/ream EVOH in layer **14**, 5

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lbs/ream nylon 6 in layer **15**, and 3 lbs/ream EVOH in layer **19**. The laminate was compared to a laminate (Comparison Sample 1) as defined in **Fig. 1** of application Serial No. 10/288,841 of which the instant application is a continuation in part comprising a paperboard substrate onto which there is applied a layer of low density polyethylene to provide the outer surface of the laminate, a polyamide polymer applied onto the interior surface of the substrate, a layer of ethylene vinyl alcohol copolymer applied to the underside of the polyamide polymer layer, a first tie layer applied to the underside of the ethylene vinyl alcohol copolymer layer, a polyolefin layer applied to the underside of the first tie layer, a second tie layer applied onto the polyolefin layer, a second layer of ethylene vinyl alcohol copolymer applied to the underside of the second tie layer, a third tie layer is applied to the underside of the second ethylene vinyl alcohol copolymer layer, followed by a polyolefin polymer layer forming the product contact surface and a laminate (Comparison Sample 2) described in Kinsey US Pat. No. 6,110,548 comprising a paperboard substrate having an outer layer of low density polyethylene, a layer of polyamide on the interior side of the substrate, a tie layer applied on the underside of the polyamide layer, a first polyolefin polymer layer applied to the underside of the tie layer, a second polyolefin polymer layer on the underside of the first polyolefin polymer layer, a second tie layer disposed on the underside of the second polyolefin polymer layer, an ethylene vinyl alcohol copolymer layer disposed on the interior of the second tie layer, a third tie layer applied on the underside of the ethylene vinyl alcohol copolymer layer and a final layer of polyolefin polymer disposed on the underside of the third tie layer.

The skived liter gable top cartons were cold filled with fresh, not-from-concentrate orange juice and stored at refrigerated (38 °F) and ambient (73 °F) temperatures across a 64 day shelf life test. Vitamin C content of the juice was measured during filling and subsequently at days 8, 21, 35, 51, and 64 after filling. Results for refrigerated and ambient storage are shown in **Fig. 3** and **4**, respectively. The packaging material of the present invention performs comparably to the Comparison Sample 1 material and better than the Comparison Sample 2 structure at both storage conditions.

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